

Renewable green polymers

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Introduction

Environmental concern and declining oil resources have led to escalated interest in producing polymers from renewable resources as an alternative to traditional oil-based commodity plastics. Different strategies are possible to build up new polymeric structures using monomers, prepolymers or polymers from nature. Several interesting monomers are available from renewable resources including aminoacids, microbial metabolites from the conversion of glucose, lactic acid, ethanol and different fatty acids. It is also possible to prepare speciality polymers from, e.g., hemicellulose prepolymers. The market of suitable short-chained plant hemicellulose material is expected to grow rapidly due to current efforts to increase the utilization of mainly xylans and glucomannans from forestry and agricultural by-products. Acetylated galactoglucomannans, AcGGM, from softwoods (Figure 1) can be obtained from steam or microwave treatment of wood and, maybe even more attractive, from residual process streams in thermomechanical pulping [1, 2].

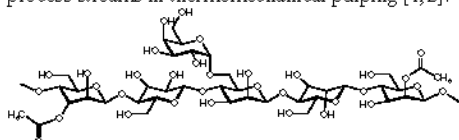


Figure 1. Illustrative fragment of AcGGM hemicellulose abundantly present in softwoods DP is about 50-100 depending on isolation etc.

The AcGGM show a strong potential in several areas. It possesses for example excellent oxygen barrier properties that can be utilized in green food packaging technology [3]. Even the drawback of the high water sensitivity might be surmountable [4]. Furthermore hydrogels (swells in water but does not dissolve) can be made consisting of predominately AcGGM [5] affecting the hydrophilicity, ion-coordination ability, physical strength, diffusional properties, bio-adaptability, renewability and biodegradability. Hence, we consider that this novel natural-based hydrogel breed may find applications in strategic areas such as pharmaceutical and medical engineering industry (drug release matrices and tissue engineering scaffolds) and agricultural industry (earth treatment, seed functionalization, etc.).

In present contribution the degradation products from PLLA are studied and specifically L-oligolactide is introduced as a part of the linker in a hemicellulose-based hydrogel..

Experimental

The procedure to produce a hydrogel involves a methacrylation of the hemicellulose carried out under mild conditions followed by radical polymerization together with 2-hydroxyethyl methacrylate (HEMA) as co-monomer [6]. Here the L-lactide was first grafted onto HEMA (Step 1 in Scheme 1) before continuing (Step 2 and 3) in the same manner as already described (citation above). HEMA and L-lactide was mixed in specific amounts under inert atmosphere and stirred at 110°C until the lactide was molten. 1mol% of Sn(oct)₂-catalyst was added dissolved in a small amount of toluene and the reaction time was set to 1h. The mixture was cooled and precipitated in ice cold water after being dissolved in THF. The precipitate was isolated, dissolved in ethyl acetate, dried over MgSO₄.

¹H-NMR was performed on a 500MHz Bruker DMX spectrometer using Bruker software. The samples were dissolved in CDCl₃ or DMSO-*d*₆ in sample tubes 5mm in diameter. FTIR spectra were recorded within a range from 4000cm⁻¹ to 600cm⁻¹ on a "Perkin Elmer Spectrum 2000" – spectrometer (Perkin Elmer Instruments, Inc.) using "Perkin Elmer Spectrum v3.02" – software.

Results and discussion

Degradation products and environmental interaction

Paralleled with the development of new materials we need to develop methods and techniques to reveal the environmental interaction and impact of the new materials (Figure 2). Small changes in the chemical structure or product formulation may change the susceptibility to degradation or cause different degradation product patterns, rendering the product less environmentally adaptable. Multiple factors affect the degradation process and it is difficult to isolate or predict the effect of individual parameters. One key question is, however, the nature of the degradation products formed, since they are released into the environment and could have negative affects. Determination of abiotic and biotic degradation products is an important step towards establishing the environmental degradation mechanism and environmental impact of the material.

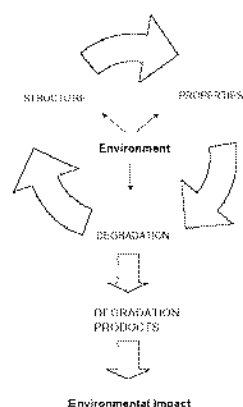
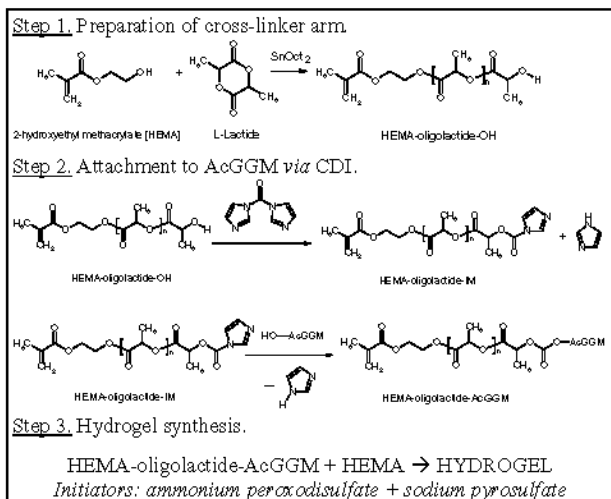


Figure 2. Polymer-Environment interactions.

We have in several studies investigated degradation and degradation products of polylactide [7,8,9,10] and other aliphatic polyesters [11,12] with the focus on determining degradation mechanisms and identification of the degradation products formed in different environments. The presence of microorganisms considerable accelerated the degradation of PLLA in aqueous environment [7]. The presence of easily assimilated low molecular weight products *i.e.* lactic acid and lactoyl lactic acid in the unaged material was important in enabling the initial growth of microorganisms on the surface of PLLA films [8]. GC-MS also revealed different degradation product patterns after biotic and abiotic degradation and showed that lactic acid and lactoyl lactic acid were rapidly assimilated in the biotic environment. Some new intermediate degradation products were detected in biotic environment *i.e.* propanoic acid and acetic acid both known fermentation products of lactic acid were identified after aging in biotic mineral medium [8].

Renewable-based hydrogels having controlled degradability

Scheme 1. The route to oligolactide-containing hemicellulose-based hydrogels.



Three different *n*s (*n* = 2, 10, 20) were produced in Step 1 (Scheme 1). An equimolar amount of AcGGM sugar units and HEMA-oligolactide-IM and 50 w-% HEMA as co-monomer were used in the

reactions. Only $n = 2$ and 10 gave acceptable products in terms of solubility after Step 2 at the charge used. The successful manufacturing of the prepolymer in Step 2 was confirmed by NMR and FTIR. In Figure 3 the FTIR spectrum of hemicellulose is compared to that of the modified HEMA-oligolactide-AcGGM and an increase of the relative absorbance was observed at the wavenumber of ~ 2950 , 1630 , and 960cm^{-1} . These wavenumbers can be assigned to the stretching and wagging of a vinyl double bond and confirmed a modification. Higher absorbance at $\sim 1100\text{cm}^{-1}$ indicate the increase in lactide-ester bonds.

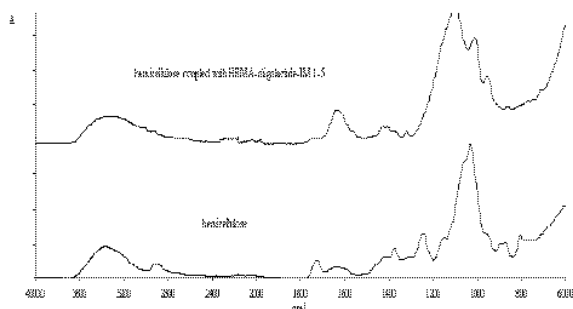
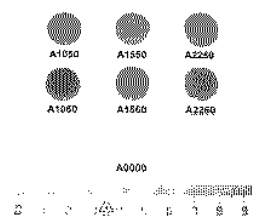


Figure 3. FTIR spectra confirming the formation of a HEMA-oligolactide-AcGGM prepolymer ($n=10$).

Hemicellulose-based hydrogels are generally very nice to handle. We have investigated them from physical point of view and the hemicellulose-part contributes to hydrophilicity, swelling, strength (eg., G modulus, rigidity, elasticity) [6]. Hydrogels including the hydrolysable oligolactide-chain could also be produced (appearance similar to A000, Figure 4) but are yet to be characterized. From a



mechanical point of view they seemed weaker than a corresponding gel without the oligolactide-spacer. The adaptability to tissue and studies of the degradation products are the next important topics and through model degradation studies on PLLA (previous chapter) and hemicellulose [13] we have already valuable knowledge about the system.

Figure 4. Synthesized hemicellulose-based hydrogels (A_{xyxy} where x %DS_{HEMA} and y w-% mod. AcGGM) and a poly(HEMA) reference gel (A000).

Conclusions

Several degradation products from PLLA were identified and their assimilation in the biotic environment was shown. Green and degradable hydrogels could be designed from renewable hemicelluloses and lactic acid.

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